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CERAMICS BASED ON REE ZIRCONATES, TITANATES, AND STANNATES

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Solid-phase synthesis of gadolinium titanate, stannate, and zirconate was investigated. It was shown that these compounds can be obtained at 700°C. A ceramic based on $Gd_2Zr_2O_7$, $Gd_2Ti_2O_7$, and $Gd_2Sn_2O_7$ was obtained. It was shown that partial substitution of Zr, Ti, and Sn(IV) for each other allows reducing the sintering temperature.

Key words: matrix material, actinoids, pyrochlores, zirconates, titanates, stannates.

In searching for materials for reliable immobilization of highly active nuclear power plant wastes (HAW), the problem of utilizing HAW with a high actinoid content has recently become especially important. This is due to the development of methods of separating HAW into fractions to immobilize them in matrices of the optimum composition. In one of the fractions obtained, the mass content of actinoids consists of tens of percent. Actinoid-containing HAW are also formed in conversion of weapons-grade plutonium [1].

High capacity with respect to radionuclides and chemical and radiation stability are the basic requirements for actinoid immobilization matrices. Compounds with the crystal structure of pyrochlore [2], in particular, REE zirconates and titanates, are considered promising materials for actinoids. Another important criterion for assessing matrix material is the technological effectiveness, i.e., the efficiency of industrial production. Uniaxial molding followed by sintering is one widespread method of matrix synthesis as it is distinguished by simplicity of equipment and low costs in comparison to other methods (for example, hot molding or induction melting). However, synthesis of $Ln_2Zr_2O_7$ from the initial oxides requires a long time (tens of hours) and high temperatures (over 1500°C) [3].

We know that using metal hydroxides or thermally unstable salts as the initial compounds allows significantly reducing the solid-phase synthesis temperature.

We obtained and investigated the properties of a ceramic based on gadolinium zirconate, titanate, and stannate and mixed zirconate-titanate, zirconate-stannate, and titanate-stannate compositions. The interest in obtained mixed compositions is due to the attempt to decrease the sintering tem-

perature of pyrochlore ceramics in partial reciprocal substitution of Zr, Ti, and Sn(IV).

A modified method based on thermal decomposition and calcinations of polyacrylamide gel containing metal salts was selected as the method for manufacturing the initial powders for synthesis of the ceramic [4]. The initial compounds were previously prepared solutions of gadolinium nitrate, zirconyl nitrate, Sn(IV) citrate, and nitric acid solution of Ti(IV) peroxide complex. Acrylamide was added to the mixed solution of metal salts and mixed until totally dissolved. The total concentration of metals in the solution obtained was 100 g/liter and the concentration of acrylamide was 250 g/liter. To eliminate the interfering effect of oxygen on radiation-induced polymerization of the acrylamide, the surface of the solution was covered with melted paraffin.

The solutions were irradiated in a RXM-γ-20 gamma unit for 24 h (GIK-7-2 cobalt sources of γ radiation, dose rate of 0.15 Gy/sec). During irradiation, radiation-induced polymerization of acrylamide took place with formation of polyacrylamide gel containing the metal salts in its pores.

The gel was pyrolyzed in a tube furnace at 450 – 500°C for 40 – 60 min. The product of pyrolysis was calcined in a muffle furnace at 750°C for 1 h with pumping of air through the furnace chamber. The powder obtained was composed of loose aggregates composed of particles with an average size of < 1 μm. The powders were disaggregated in a ball mill in aqueous medium for 3 h (ball : material : water ratio = 30 : 1 : 1). According to the results of laser-diffraction measurements, 90% of the particles were no greater than 1.5 μm in size.

A 5% solution of polyvinyl alcohol (mass content of 2 – 2.5% in terms of dry powder) was added to the solution and dried at 100°C to a residual moisture content of 10%. The prepared powders were molded by uniaxial molding at a

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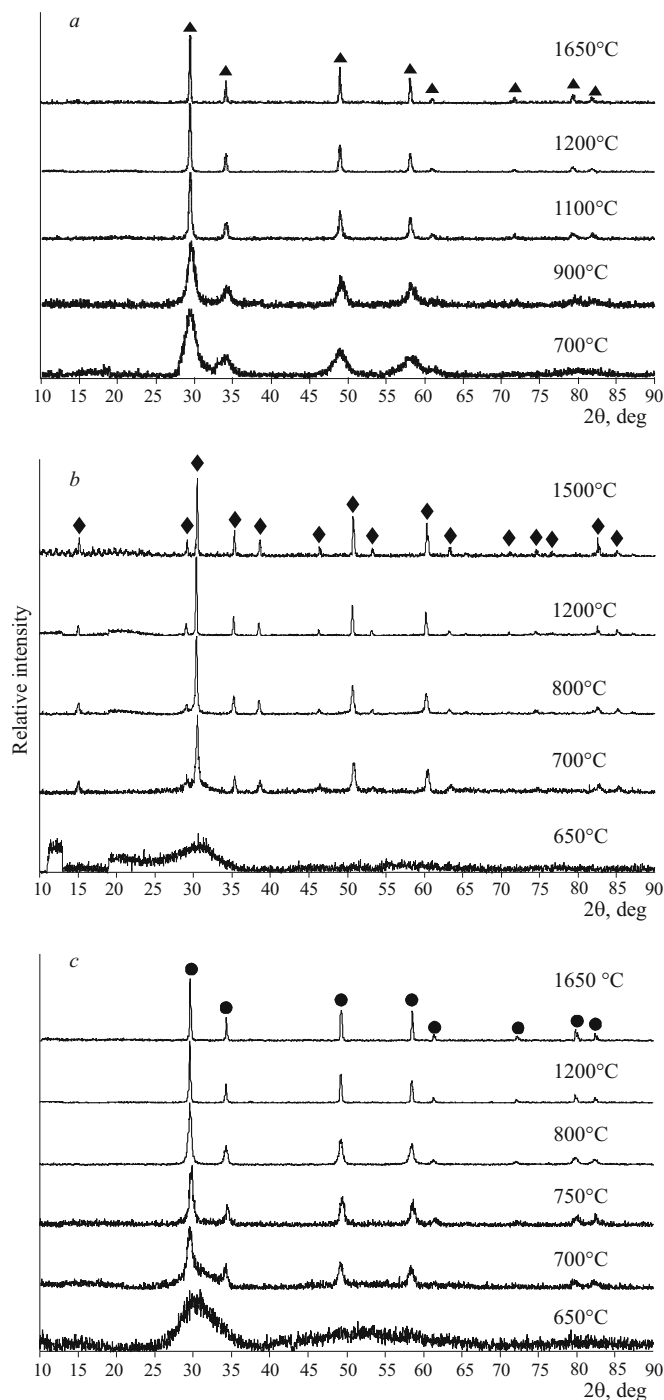
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Fig. 1. X-ray diffractograms of powers of $Gd_2Zr_2O_7$ (*a*), Gd_2TiO_7 (*b*), and $Gd_2Sn_2O_7$ (*c*) after heat treatment: ▲) cubic phase of $Gd_2Zr_2O_7$; ◆) cubic phase of Gd_2TiO_7; ●) cubic phase of $Gd_2Sn_2O_7$.

pressure of 580 MPa. The samples prepared for firing were in the shape of cylindrical pellets 1 – 2 mm thick and 12.0 mm in diameter. The stock was fired at different temperatures. The heating rate in all cases was 300 K/h, and the isothermal holding time was 3 h.

The x-ray phase analysis of the initial powders fired for 1 h at different temperatures showed that the target gadoli-

nium zirconate, titanate, or stannate phases were already formed at 700°C (Fig. 1). The crystal lattice was completed when the temperature was increased further, as indicated by the decrease in the noise level of the diffractograms and the decrease in the width of the reflections. No reflections of the individual ZrO_2, TiO_2, SnO_2, and Gd_2O_3 oxides were found in any of the diffractograms.

The previous history of heat treatment of the initial powder has an important effect on the behavior of molded samples in sintering. A series of experiments with powders of the stoichiometric compositions $Gd_2Sn_2O_7$, Gd_2TiO_7, and $Gd_2Zr_2O_7$ was conducted to find the optimum temperature of preliminary calcination. After pyrolysis of the polyacrylamide gel and burning off carbon at 700 – 750°C, the powders were additionally held for one hour at different temperatures (from 700 to 1200°C). Disaggregation of the powders, molding, and sintering of the stock were then conducted as described above.

The results of measuring the open porosity P_o and relative density ρ_{rel} of the ceramic obtained (see Table 1) show that the optimum temperature of preliminary heat treatment of $Gd_2Zr_2O_7$ powder does not exceed 1000 – 1100°C. Sintering of the pellets in this case results in a ceramic with zero open porosity and density of 99 – 100% of the theoretical at the sintering temperature of 1550 – 1600°C. Increasing the preliminary calcination temperature of the powder to 1200°C slightly worsens the properties of the ceramic sintered in the same conditions.

For $Gd_2Sn_2O_7$ powders, the dependence of the density of the ceramic at a fixed sintering temperature (1650°C) on the preliminary heat treatment temperature of the powder attains the maximum (93% of the theoretical) at 1100°C. The open porosity at the same heat-treatment temperature attains the minimum (0.9%). This dependence also holds at the other sintering temperatures.

The optimum preliminary calcination temperature of Gd_2TiO_7 is 1100°C. Sintering at 1400°C allows obtaining a ceramic with zero open porosity and a density of up to 94% of the theoretical. This is slightly lower than the density of the ceramic obtained in the same conditions from powder calcined at 1000°C (99%). This finding can also indicate the greater sinterability of powder previously calcined at 1100°C, which results in the earlier appearance of open pores and slowing of compaction of the ceramic.

The sinterability of the mixed zirconate-titanate, zirconate-stannate, and stannate-titanate ceramic was investigated. We found that substitution of up to 40% of the molar content of tin in gadolinium stannate by titanium did not significantly reduce the sintering temperature (Fig. 2). The open porosity decreased to a value of less than 1%, while the density attained 93 – 95% of the theoretical only at 1650°C. Increasing the titanium content to 60% ($x = 0.8$) decreased the sintering temperature by 200°C. The ceramic of the compositions $Gd_2Sn_{0.8}Ti_{1.2}O_7$ and $Gd_2Sn_{0.4}Ti_{1.6}O_7$ with zero open po-

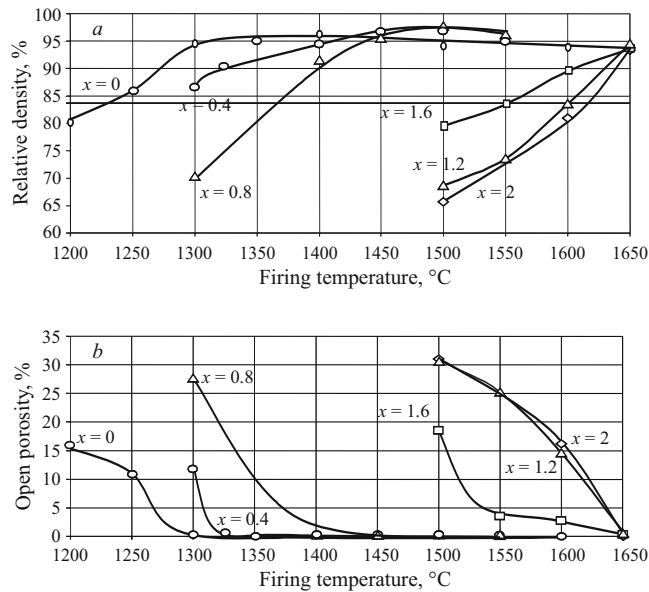**Fig. 2.** Relative density (*a*) and open porosity (*b*) of stannate-titanate ceramic $Gd_2Sn_xTi_{2-x}O_7$ as a function of firing temperature.

Fig. 3. Relative density (*a*) and open porosity (*b*) of zirconate-titanate ceramic $Gd_2Zr_xTi_{2-x}O_7$ as a function of firing temperature.

rosity and density of up to 97 – 98% of the theoretical value can be obtained at 1450 – 1500°C.

Substitution of 20% of the molar content of zirconium in gadolinium zirconate by titanium ($x = 1.6$) results in a ceramic with zero open porosity and density close to the theoretical at 1475 – 1500°C (Fig. 3). A further increase in the titanium content to 60% of the molar content ($x = 0.8$) did not significantly decrease the sintering temperature. Note that incorporation of > 50% of the molar content of titanium decreased the radiation stability of the material [5]. A maximum titanium content of 20% of the molar content should probably be considered optimum. The sintering temperature
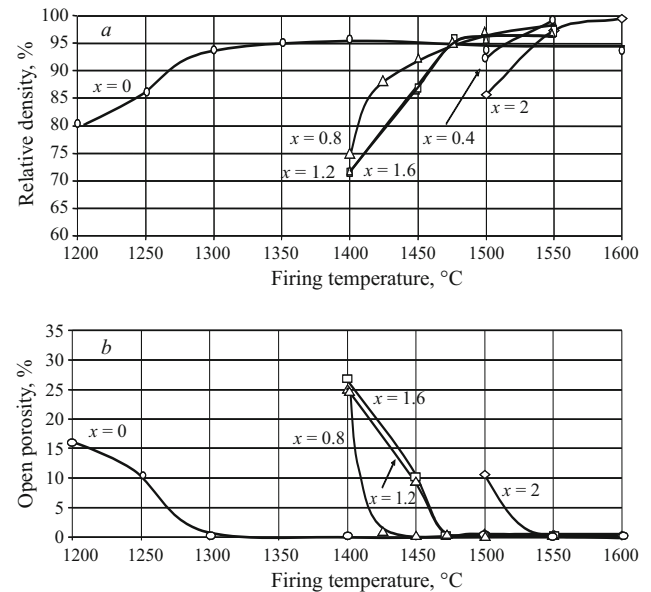
of this ceramic did not exceed 1475°C, which is 75°C lower than for the pure zirconate and 150 – 200°C higher than for gadolinium titanate.

Despite the fact that the sintering temperature of pure gadolinium stannate is 100 – 150°C higher than for the zirconate, incorporation of tin in $Gd_2Zr_2O_7$ decreases the sintering temperature of the latter (Fig. 4). Substitution of 60% of the zirconium molar content by tin ($Gd_2Zr_{0.8}Sn_{1.2}O_7$) was most effective. The ceramic of this composition with zero open porosity can be obtained at 1450°C.

We can thus conclude that substitution of zirconium in gadolinium zirconate by titanium (20%) or tin (60%) and tin

TABLE 1. Properties of the Ceramic after Firing as a Function of Heat Treatment of the Powder

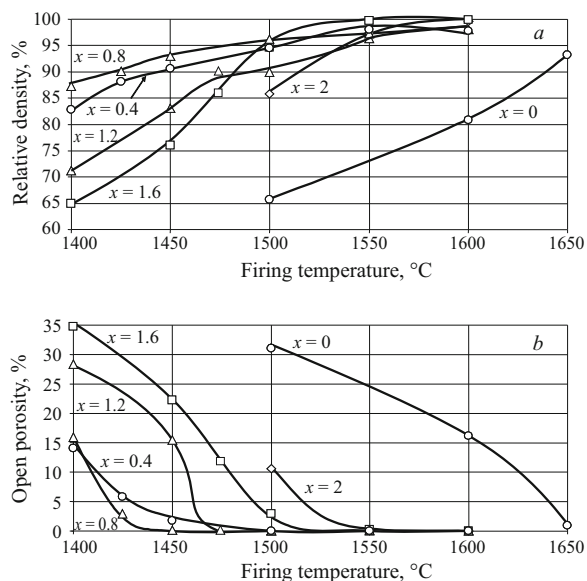| Composition	Sintering temperature, °C	Temperature of preliminary heat treatment of initial powder							
		700°C		1000°C		1100°C		1200°C	
		P_o, %	ρ_{rel}, %	P_o, %	ρ_{rel}, %	P_o, %	ρ_{rel}, %	P_o, %	ρ_{rel}, %
$Gd_2Zr_2O_7$	1500	19.7	78	10.6	86	12.9	86	21.8	78
	1550	–	–	0.0	97	–	–	2.5	93
	1600	4.5	91	0.0	~ 100	0.0	99	0.0	98
	1650	0.0	95	–	–	0.0	99	–	–
$Gd_2Sn_2O_7$	1500	43.1	53	34.7	65	31.0	66	31.7	67
	1600	36.7	62	25.4	75	16.1	81	17.4	81
	1650	24.7	74	14.7	84	0.9	93	8.8	89
$Gd_2Ti_2O_7$	1200	–	–	16.0	80	16.8	80	32.0	65
	1250	–	–	16.2	83	11.1	86	30.4	67
	1300	–	–	5.1	88	0.1	94	23.8	74
	1350	–	–	0.2	96	0.0	95	12.3	85
	1400	–	–	0.0	99	0.0	94	0.0	97

Fig. 4. Relative density (*a*) and open porosity (*b*) of zirconate-stannate ceramic $Gd_2Zr_xSn_{2-x}O_7$ as a function of firing temperature.

in gadolinium stannate by titanium (60 – 80%) or zirconium (40%) allows reducing the temperature of production of a nonporous, dense ceramic by 150 – 300°C.

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